



Development of Passive HC/NO_x Trap Catalysts for Low Temperature Gasoline Applications

Project ID #: ace130

Mark Crocker
University of Kentucky
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Overview

Timeline

- Project start date: 9/1/17
- Project end date: 8/31/20
(now 11/30/20)
- **Percent complete: 70%**

Budget

- Total project funding
 - DOE share: \$2,098,350
 - Contractor share: \$300,614
- Funding for FY 2018: \$845,015
- Funding for FY 2019: \$743,731
- Funding for FY 2020: \$810,218

Barriers and Technical Targets

- Barriers addressed:
 - Improve low temperature and cold start NOx control
 - Improve low temperature and cold start HC control
 - Characterize and understand Passive NOx Adsorber (PNA) durability

Partners

- Collaboration: Ford, ORNL, Purdue, UC Berkeley, BASF
- Project lead: U. Kentucky

Relevance

Impact

- Improved Pd/zeolite HC/NO_x adsorbers will enable vehicle manufacturers to satisfy future emission standards and improve vehicle fuel economy by reducing cold start fueling requirements

Objectives

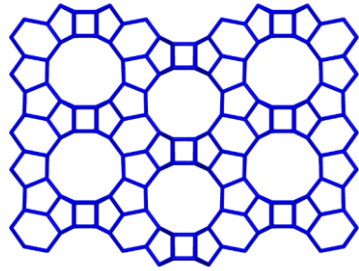
- Fundamental understanding of the chemistry of NO_x adsorption and reduction in Pd/zeolites will be attained
- Pd/zeolites will be tailored with respect to performance and durability for application as HC/NO_x adsorbers
- HC/NO_x adsorber performance will be validated using exhaust gas from an engine dynamometer
- Scientific insights and technology will be transferred to the automotive industry via the project's industry partners

While this technology should be applicable to both gasoline and diesel vehicles, gasoline applications are emphasized in this project, given the importance of stoichiometric engines in the U.S. automotive market

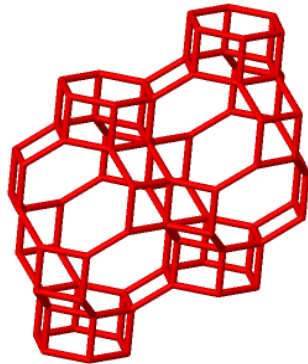
Milestones for FY2020

Task	Date	FY2020 Milestone Description	Status
Reactor studies	2/28/20	Steady state kinetics of NO reduction by C ₂ H ₄ and CO determined for Pd/CHA and Pd/BEA	On-going
Catalyst characterization	5/31/20	Structure-property relations between Pd site types, spectroscopic features, and NO/HC adsorption behavior elucidated	On-going
Reactor studies	8/31/20	Cold start performance of Pd/CHA and Pd/BEA evaluated under simulated stoich. gasoline, lean burn gasoline and diesel exhaust	On-going
Computational studies	11/30/20	Energy and free energy landscapes for reactions of coadsorbed NO/CO, NO/ C ₂ H ₄ , & NO/CH ₃ C ₆ H ₅ derived for Pd/CHA and Pd/BEA	On-going
Catalyst aging studies	11/30/20	Mechanism of Pd/zeolite catalyst degradation under hydrothermal aging elucidated	On-going
Prediction of vehicle performance	11/30/20	Impact of new catalyst on tailpipe emissions estimated using vehicle emission model	To be done
Catalyst performance validation (Go/no-go)	11/30/20	Optimized HC/NO adsorber catalyst validated using engine exhaust: NO adsorption and high temperature retention (up to 300 °C) superior to Pd/CeO ₂ -ZrO ₂ after 50 h 4-mode aging	To be done

Approach



Beta (BEA)



Chabazite (CHA)

- Use combination of experimental and computational methods to allow a deeper understanding of the governing chemistry in Pd-zeolite PNAs
- Pd-CHA as (relatively!) simple system amenable to study, Pd-Beta as commercially relevant system
- Focus in Years 1 and 2 on understanding how framework type, SAR, Al distribution, etc., impact NO adsorption and desorption behavior
- Focus in Year 3 on design of optimized system and assessment of durability

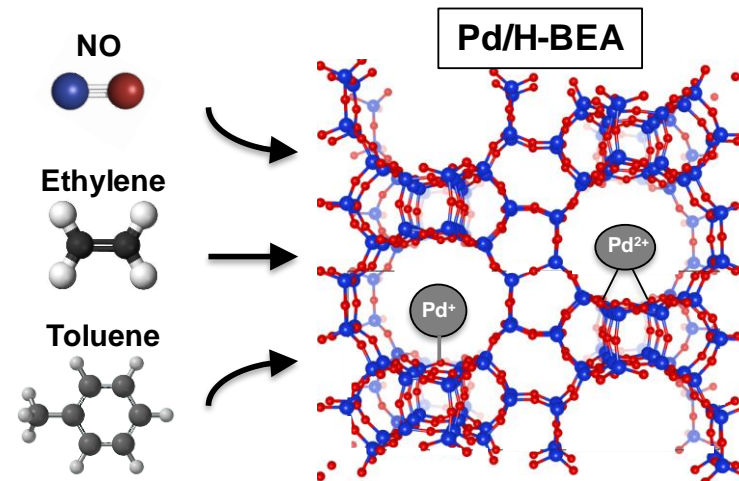
Collaboration

- **UK** (Mark Crocker):
Project management, spectroscopic studies (DRIFTS, ESR, XPS), catalyst aging
- **Purdue** (Raj Gounder):
Zeolite/catalyst synthesis, catalyst characterization, spectroscopic studies (XAS)
- **UC Berkeley** (Alex Bell):
NOx/HC adsorption/desorption and kinetic studies, computational studies
- **Ford** (Christine Lambert):
NOx/HC adsorption/desorption studies, catalyst evaluation, emissions modeling
- **ORNL** (Vitaly Prikhodko):
Catalyst characterization (TEM), catalyst aging, catalyst evaluation (slip stream from engine test bench)
- **BASF** (Xinyi Wei):
Catalyst preparation (zeolites)

Technical Accomplishments

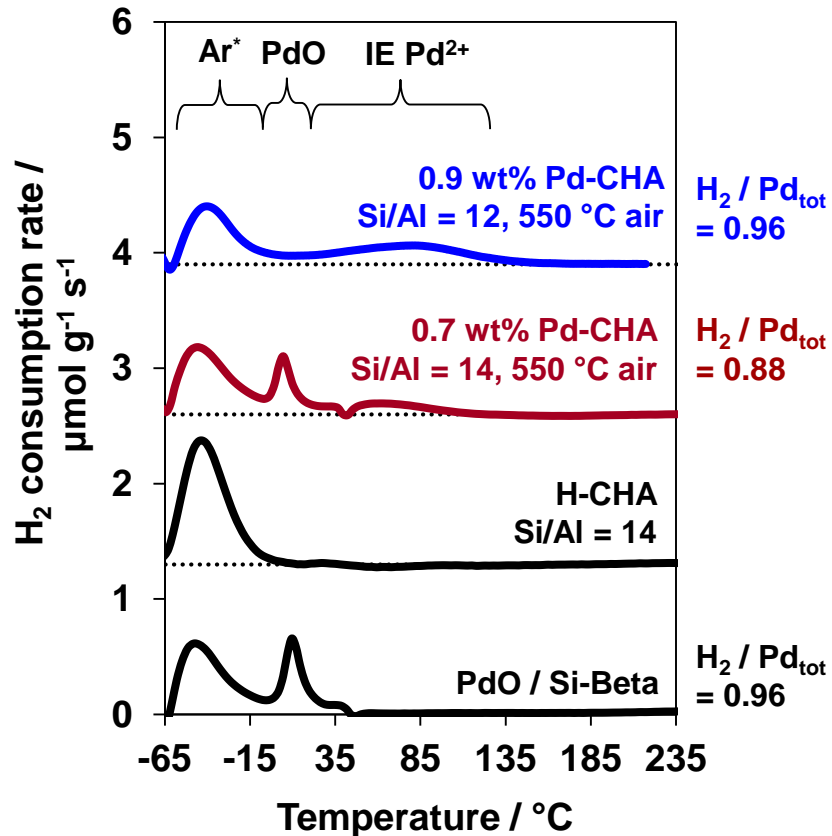
Work focused in five main areas to date:

- Pd-CHA and Pd-Beta synthesis and characterization
- Microreactor studies of NO adsorption and desorption
- Pd-CHA evaluation in simulated cold start tests
- Spectroscopic studies (DRIFTS, DRUVS, XAS, XPS) studies to characterize Pd speciation and NO adsorption sites
- Computational studies to characterize Pd speciation and NO adsorption sites



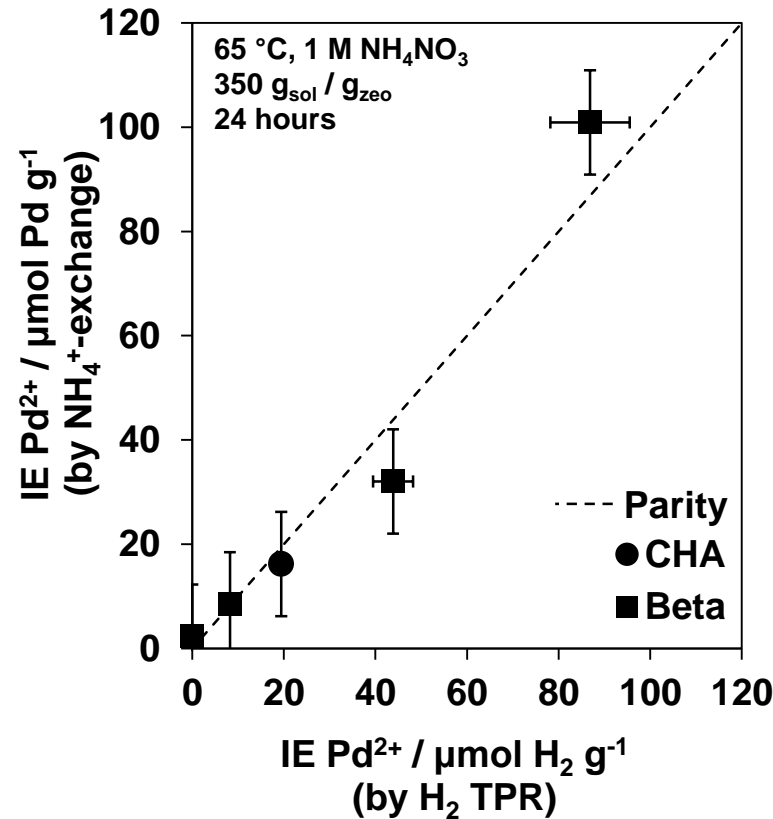
Methods for Characterizing Pd-exchanged Zeolites

H₂ Temperature Programmed Reduction (TPR)



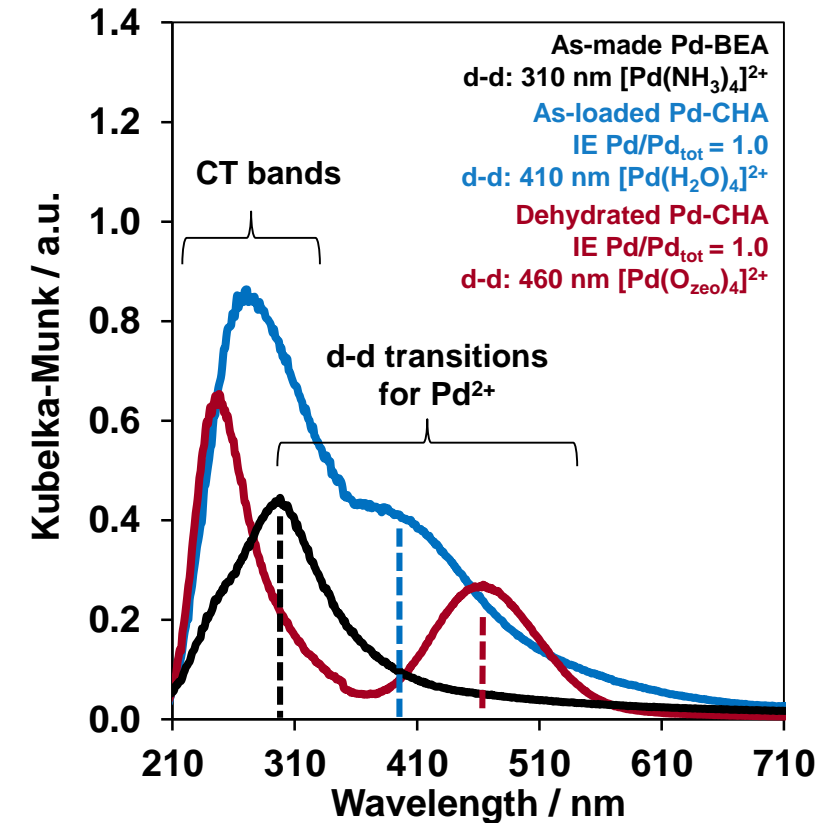
- H₂ TPR can quantify PdO and ion-exchanged (IE) Pd²⁺
- H₂ / Pd_{tot} consumptions are consistent with predominantly divalent Pd²⁺

NH₄⁺-back exchange



- Pd contents in NH₄⁺ back-exchange supernatants match IE Pd²⁺ measurements using H₂ TPR

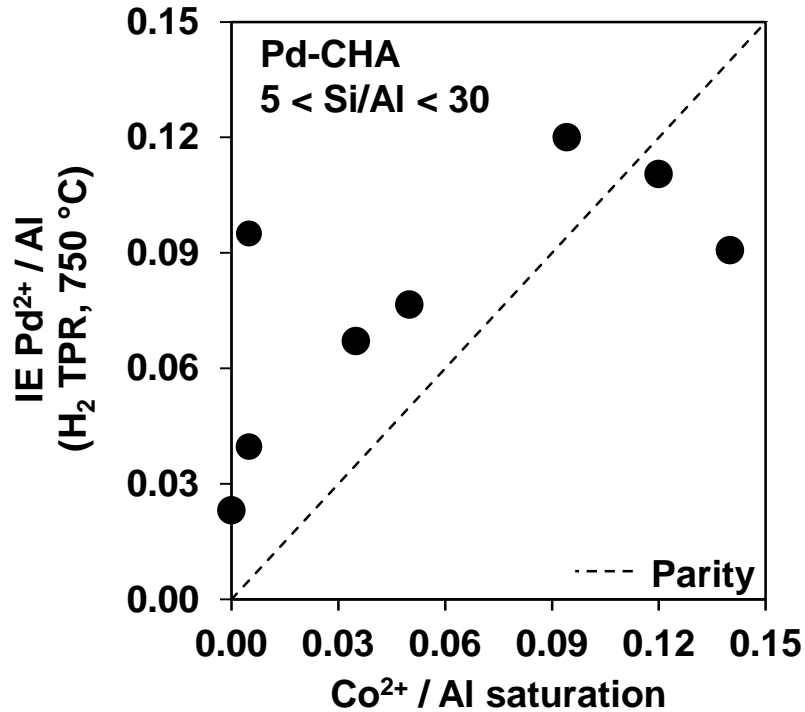
Diffuse Reflectance Ultraviolet-Visible (DRUV-Vis) Spectroscopy



- *In-situ* DRUV-Vis can be used to probe the ligand environment around ion-exchanged Pd²⁺

Identifying Exchanged Pd Structures and H₂ TPR/re-oxidation Cycles

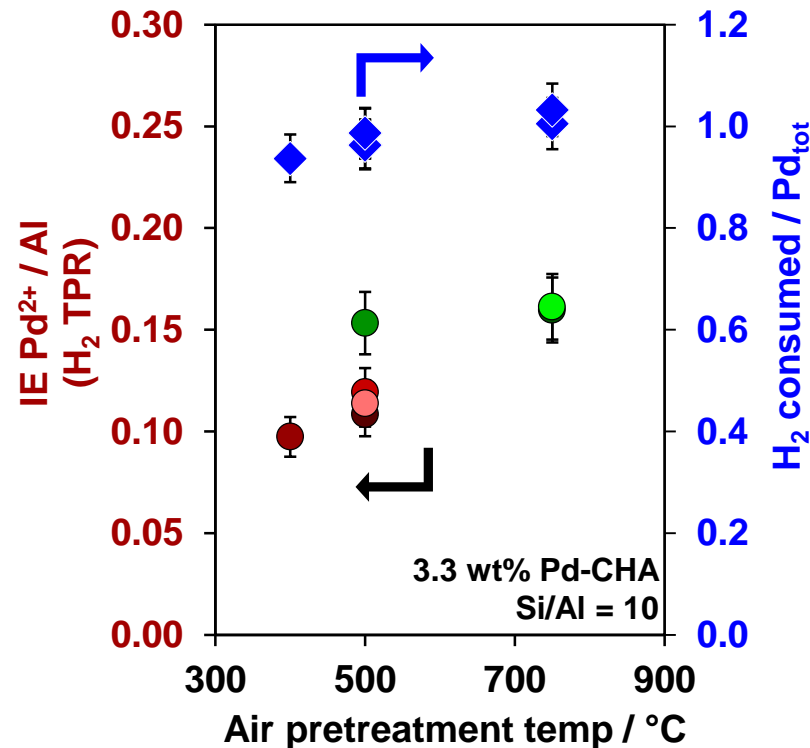
Pd structures



- Co²⁺ saturation isotherms have been reported to measure the density of two Al sites in the 6 MR of CHA zeolites*
- EXAFS spectra of hydrated samples show Pd²⁺ sites are site-isolated (no second-shell scatter)
- No correlation above suggests both Pd²⁺ and Pd⁺/[PdOH]⁺ are potential ion-exchanged species

H₂ TPR/re-oxidation cycles

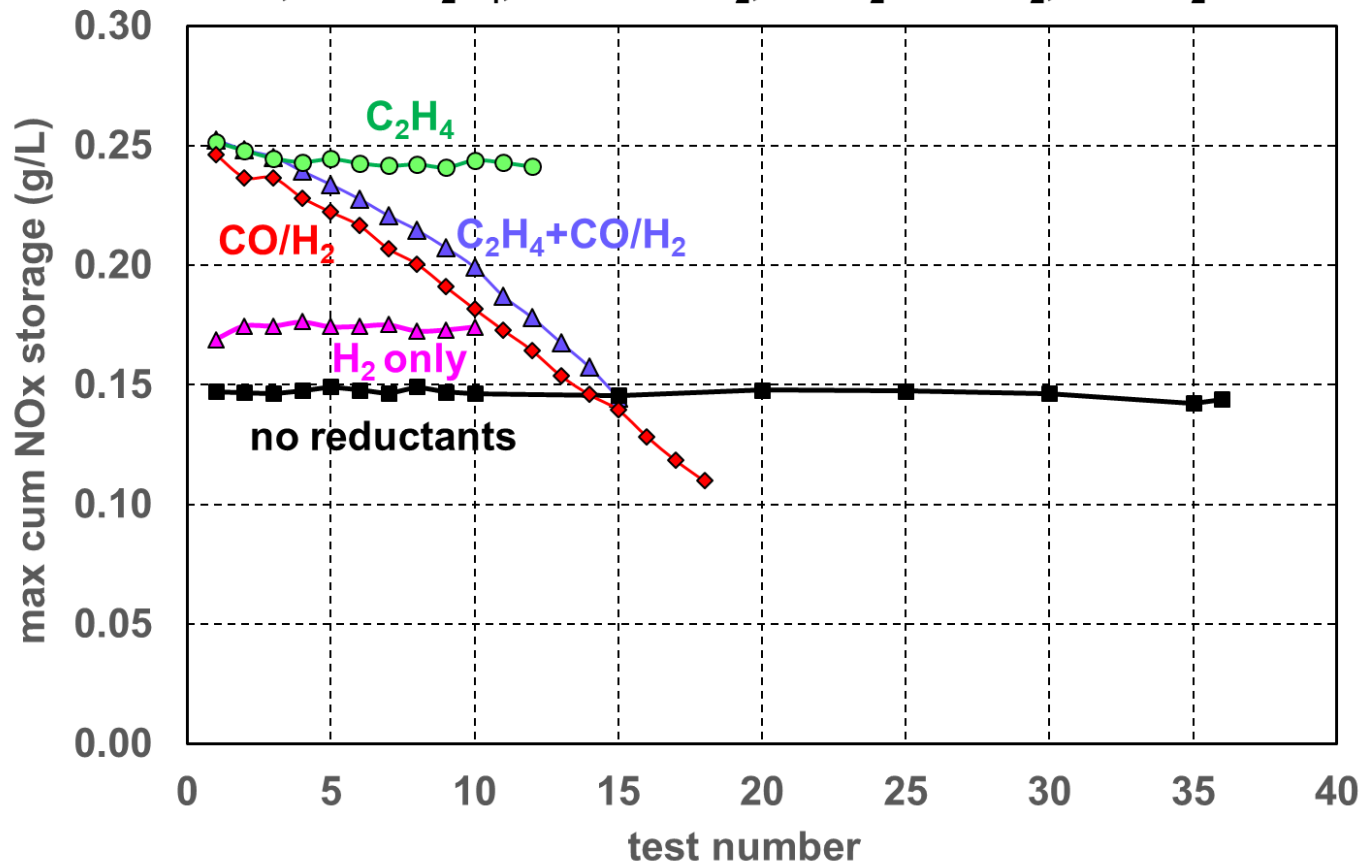
Cycle	Dry Air Temp (°C)	H ₂ / Pd _{tot}	PdO / Pd _{tot}	IE Pd ²⁺ / Pd _{tot}	IE Pd ²⁺ / Al
1	500	0.97	0.52	0.45	0.11
2	400	0.94	0.54	0.45	0.10
3	500	0.99	0.50	0.49	0.12
4	500 (+2% H ₂ O)	0.96	0.50	0.47	0.11
5	750	1.01	0.35	0.66	0.16
6	500	0.99	0.36	0.63	0.15
7	750	1.03	0.37	0.66	0.16



- Cycles 1-4** resulted in similar amounts of IE Pd²⁺, demonstrating Pd metallic nanoparticles (300 °C, 5% H₂) are re-dispersed in air (400-500 °C) to similar final states
- After a 750 °C treatment, cycles 5-7** resulted in higher amounts of ion-exchanged Pd²⁺
- 750 °C air treatments are hypothesized to more homogeneously distribute Pd throughout the sample**

Progressive Deactivation of CHA-based PNA is Caused by CO

Max NO_x storage, CHA 125 gpcf Pt/Pd at 1/4, ~470 C max bed T
110 NO, w/wo C₂H₄, w/wo CO/H₂, 5% H₂O & CO₂, 10% O₂



Consecutive NO storage and release tests

Storage at 90°C, then ramp to 470°C in feedgas

Cool in 10% O₂ between tests

Tests with 110 ppm NO w/o reductant

And with:

900 ppm CO + 300 ppm H₂

Or with:

1000 ppm H₂

Or with:

150 ppm C₂H₄

Or with:

150 ppm C₂H₄ + 900 ppm CO + 300 ppm H₂

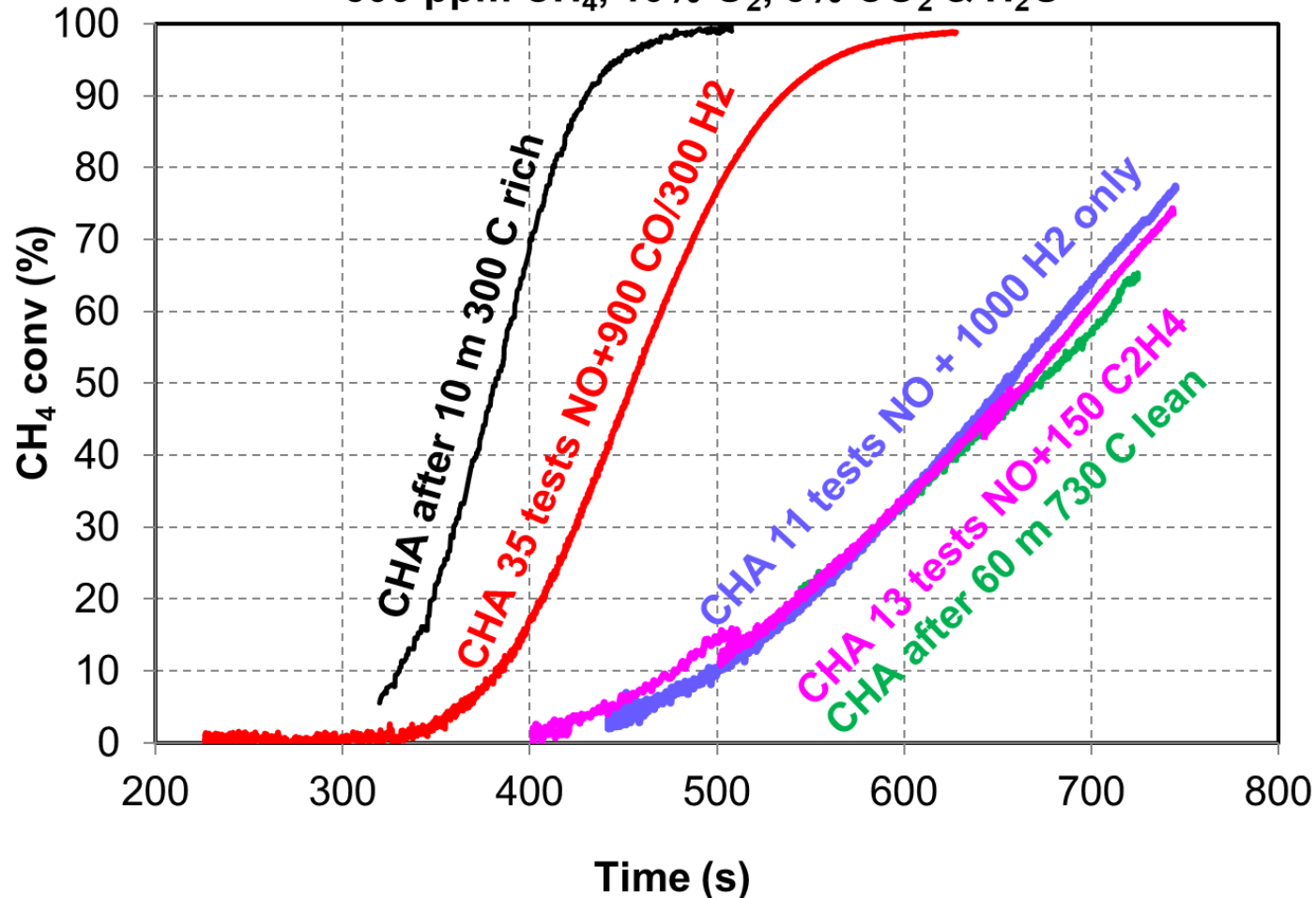
➤ NO_x capacity drops on tests with CO, not on tests without reductant or on tests with C₂H₄ or H₂

Deactivation Due To Reduction of Palladium

Methane LO test to probe Pd oxidation state

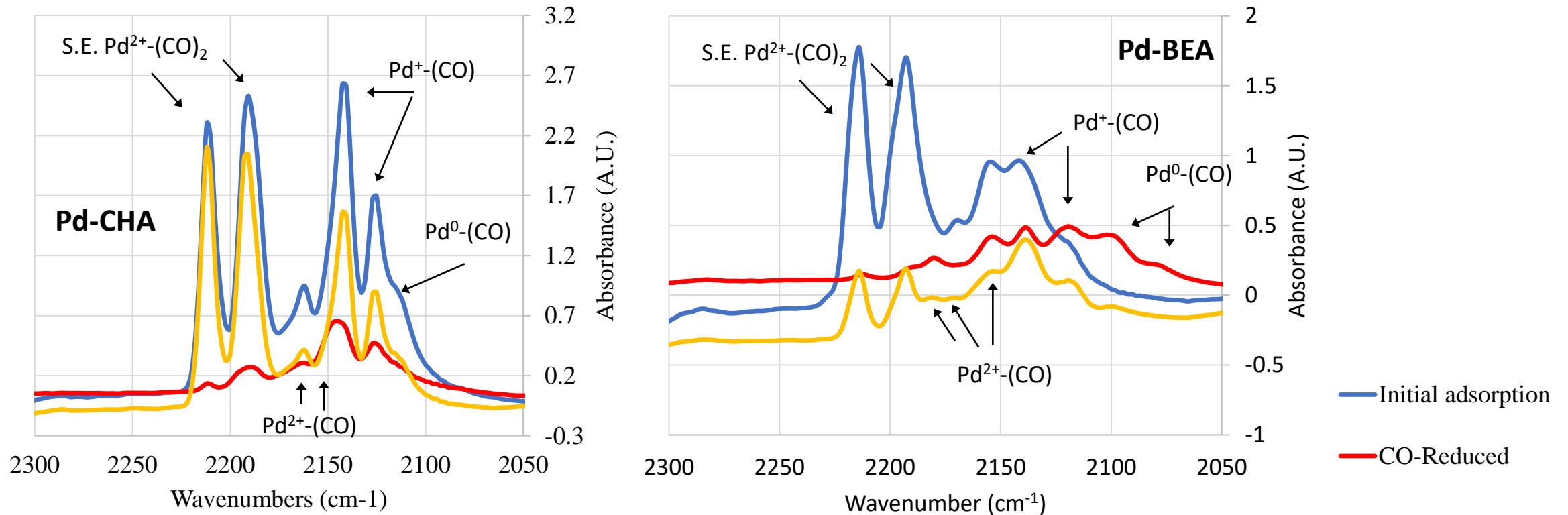
CHA 125 gpcf Pt/Pd @ 1:4

500 ppm CH₄, 10% O₂, 5% CO₂ & H₂O



- Methane light-off is sensitive to palladium oxidation state
 - Reduced palladium is active for methane oxidation ($T_{50} \sim 370^{\circ}\text{C}$)
 - Oxidized / exchanged palladium has comparatively low activity
 - ($T_{50} \sim 650^{\circ}\text{C}$)
- After CO exposure, palladium is mostly reduced
 - Exposure to H₂ or C₂H₄ does not reduce palladium

Effect of CO Reduction on Pd-Speciation in 1% Pd-CHA and 1% Pd-BEA



Samples treated in (i) dry Ar; (ii) 1000 ppm CO in Ar; (iii) dry air at 500 °C. CO adsorbed at 25 °C for 10 min

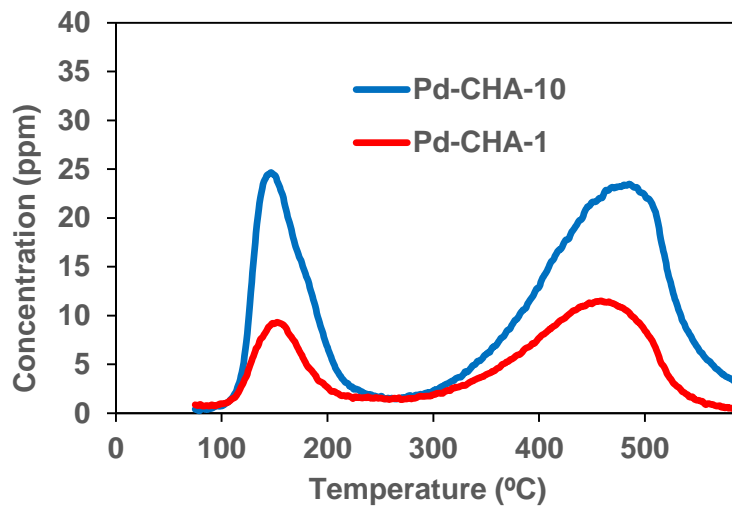
- Retention of ionic Pd after CO reduction at 500 °C: Pd-CHA > Pd-BEA
- Recovery of S.E. Pd²⁺ after re-oxidation of CO reduced catalysts: Pd-CHA > Pd-BEA
- Metallic Pd-CO bands (< 2000 cm⁻¹) indicate formation of external Pd particles after reduction
- Nearly all metallic Pd eliminated after re-oxidation

Effects of Amount of Isolated Pd and Water Vapor on NO Adsorbed on Pd-CHA

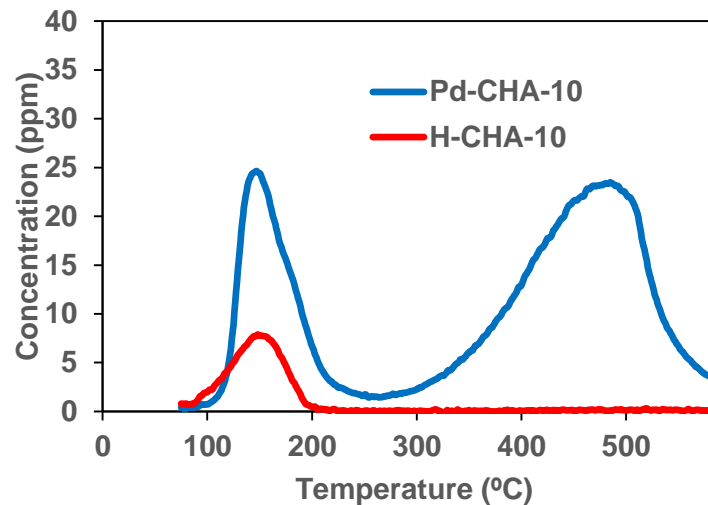
Methodology

- **Pre-treatment:** Oxidize in air (20% O₂) and 5% H₂O at 500 for 5 h
- **Adsorption:** Adsorb NO (200-400 ppm in He) at 75°C
- **Desorption:** Temperature-programmed desorption (TPD) 75°C to 500°C at 10°C/min in flowing He
- **Post-treatment (between adsorption cycles):** Cool catalysts (from 500°C to 75°C) after TPD in He containing 5% H₂O

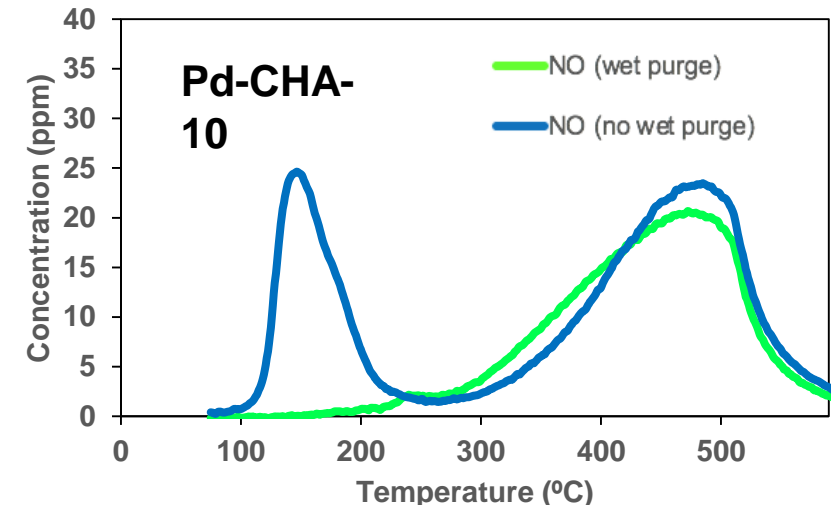
NO TPD – Pd-CHA without water exposure after NO adsorption



NO TPD – H-CHA-10 and Pd-CHA-10 without exposure to water vapor after NO adsorption



NO TPD – Pd-CHA-10 with/without water exposure after NO adsorption

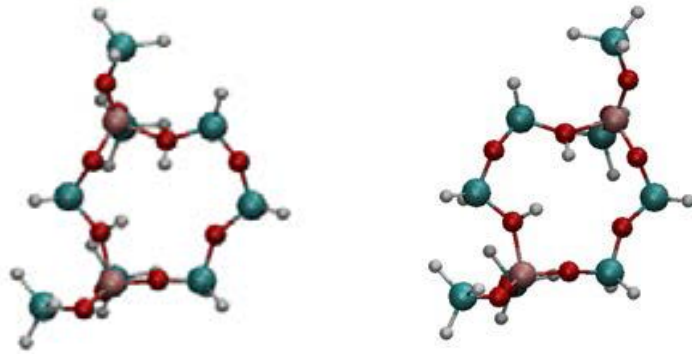


- Increasing the weight percentage of isolated Pd from 0.18 wt% in Pd-CHA-1 to 0.66 wt% in Pd-CHA-10 increases the amount of weakly and strongly adsorbed NO

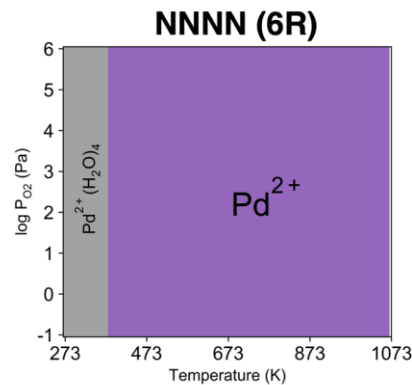
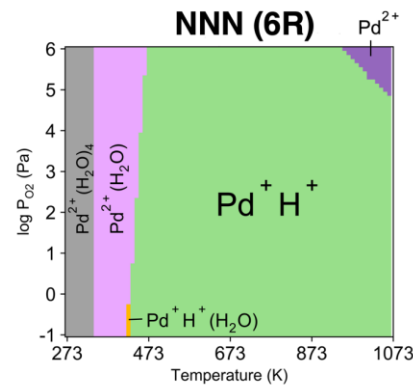
- Amount of NO desorbing at 150°C is greater for Pd-CHA-10 than H-CHA-10

- Passage of water vapor following NO adsorption at 75°C displaces NO that would desorb at 150°C
- NO desorption at 475°C occurs on Pd-CHA-10 and is not displaced by water vapor

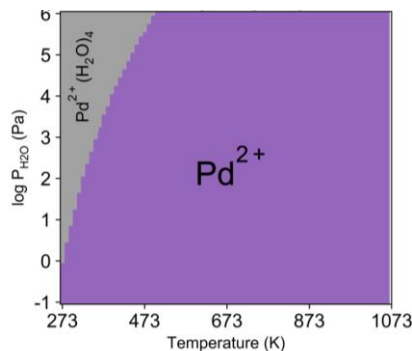
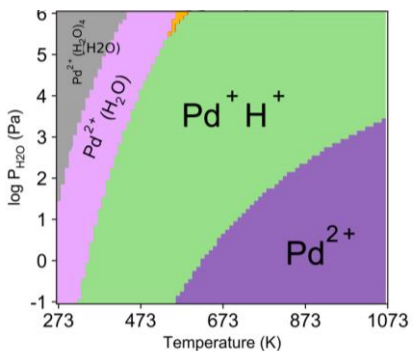
Effect of Water on Pd Speciation at Al Pairs in CHA by QM/MM



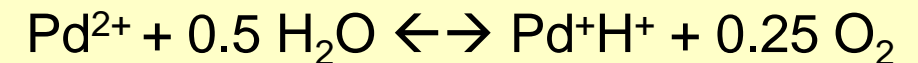
[log P_{O_2} , T]
diagrams
 $P_{H_2O} = 5 \text{ kPa}$



[log P_{H_2O} , T]
diagrams
 $P_{O_2} = 20 \text{ kPa}$



- At a given temperature, Pd speciation is much **more sensitive** to P_{H_2O} than P_{O_2}
- Pd^{2+} at **NNNN(6R) Al pair** is thermodynamically most favorable over a wide range of conditions
→ **unchangeable**
- Equilibrium between Pd^+ and Pd^{2+} at **NNN(6R) Al pair** depends on conditions
→ high T treatment in 5% H_2O promotes formation of Pd^+



Competitive Adsorption of NO, CO, H₂O and C₂H₄ on Pd Cation Sites

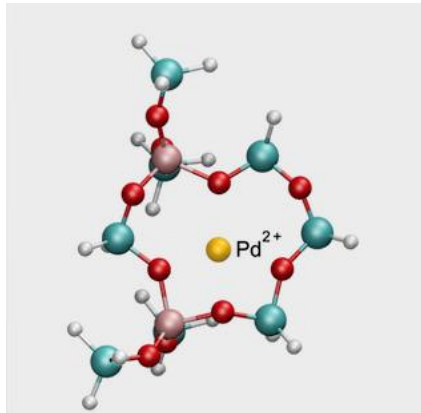
- Calculated adsorption thermodynamics: $\Delta G_{\text{ads},i} (T, P_i)$ $P_{\text{H}_2\text{O}} = 5 \text{ kPa}$; $P_{\text{NO}} = P_{\text{CO}} = P_{\text{C}_2\text{H}_4} = 20 \text{ Pa}$

$\Delta G_{\text{ads},i} < 0$: adsorption **favorable**
 $\Delta G_{\text{ads},i} > 0$: adsorption **unfavorable**

desorption temperature? $\rightarrow \Delta G_{\text{ads},i} (T, P_i) = 0$

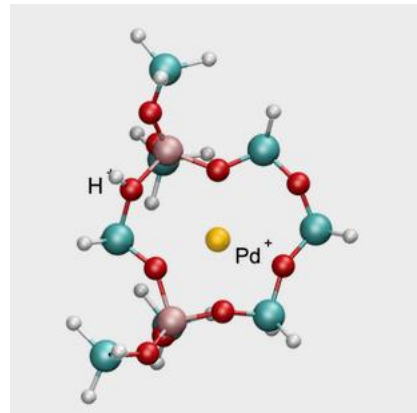
- For different potential adsorption sites: relative adsorption strength; estimated desorption temperature (°C)

Pd²⁺ (NNN)



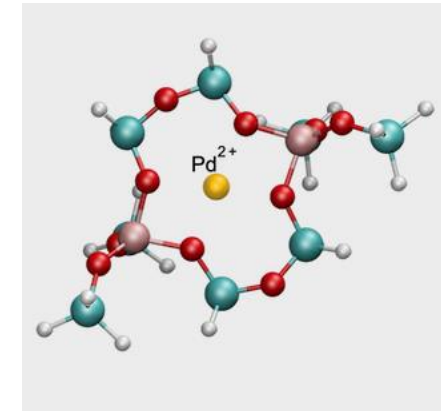
H₂O > NO > C₂H₄ > CO
 250°C 175°C -80°C -150°C

Pd⁺ H⁺ (NNN)



NO > CO > C₂H₄ > H₂O
 400°C 300°C 225°C 175°C

Pd²⁺ (NNNN)



NO > C₂H₄ > H₂O > CO
 30°C -100°C -150°C -170°C

Low T NO desorption peak seen in TPD experiments is attributed to Pd²⁺ (NNN) sites
 High T NO desorption peak seen in TPD experiments is attributed to Pd⁺H⁺ (NNN) sites

Responses to Previous Year Reviewers' Comments

- The project appears to be progressing well, though it was somewhat unclear to the reviewer whether the milestones are on track. For instance, the reviewer noted that the status of spectroscopic studies, which has a date in the past, is “Done/on-going.” The reviewer asked whether this implies that the milestone has been met but additional work is being done in the area.
 - The reviewer is correct: We’ve essentially done what we said we would do, but spectroscopic studies are continuing because of the complexity of the system: as we learn more from the computational studies, etc., ideas for additional spectroscopic experiments arise
- The reviewer said that it will be useful to look at the degradation mechanism identified in this work.
 - Done: work by Ford suggests that degradation can be attributed to a slow reduction of Pd^{n+} by CO, to give Pd^0 . DRIFTS data supports this view.

Remaining Challenges and Barriers

- Understanding the exposure conditions and mechanisms for Pd mobility in zeolites (Pd sintering, Pd re-dispersion, nature of mobile Pd species)
- Identifying the adsorption sites corresponding to different forms of adsorbed NO observed during temperature programmed desorption (correlation of spectroscopic data, DFT calculations and microreactor data)
- Understanding the chemistry whereby Pd⁺ sites are formed, such that NO adsorption can occur
- Degradation upon extended cycling is a major barrier to practical implementation – the development of a viable regeneration strategy is critical
- Cost of Pd and volatile markets

Future Work

On-going

- Explore how Al distribution impacts NO_x storage capacity and catalyst durability (CHA with different amounts of paired Al sites prepared)
- Characterize the redox chemistry associated with NO adsorption on Pd²⁺
- Explore whether viable reactivation strategies exist for recovering catalyst performance

Planned

- Monolithic Pd/CHA catalyst evaluation in engine exhaust
- Vehicle level modeling of PNA emission reduction benefits

Any proposed future work is subject to change based on funding levels

Summary

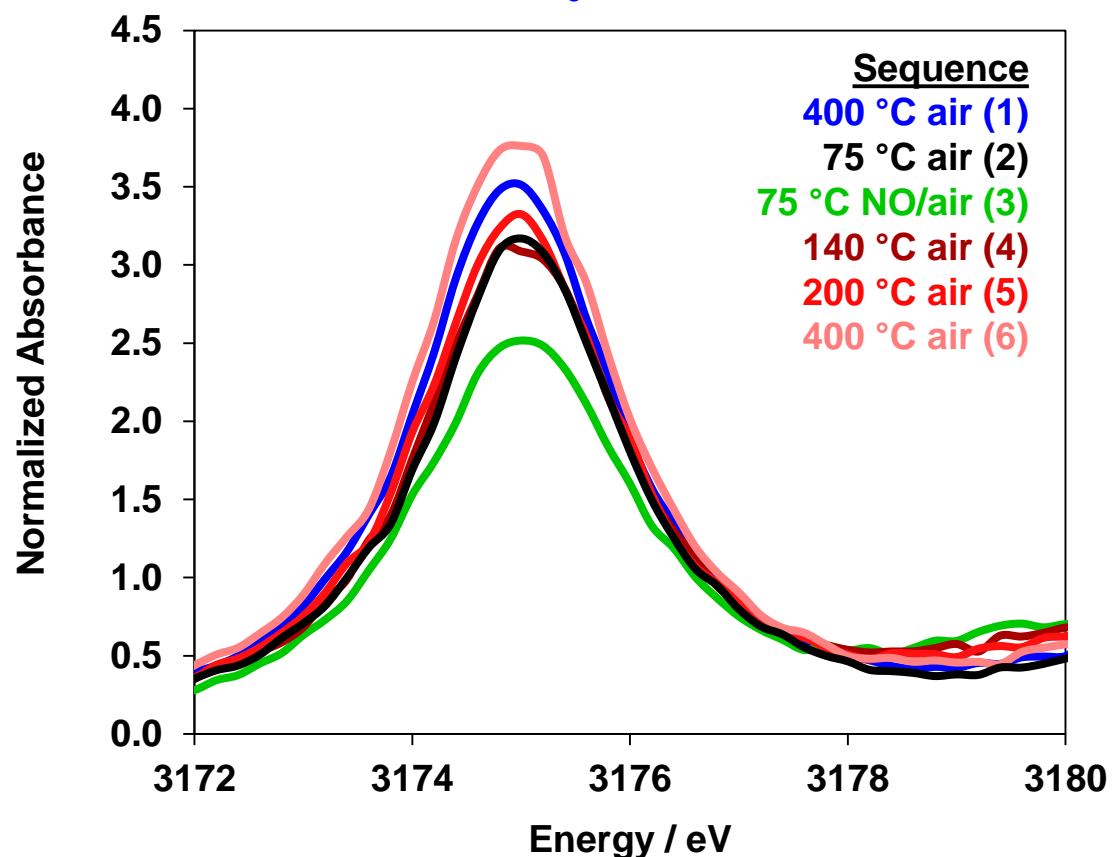
- Progressive deactivation of CHA-based PNAs during repeated adsorption/desorption cycles is caused by CO
- H₂O, H₂ and CO all act as reducing agents on Pd-zeolites
- Pd-CHA is more resilient to reduction than Pd-BEA
- CO has strongest reducing effect, inhibits re-dispersion of Pd due to formation of bulk Pd
- H₂O and H₂ behave similarly: pore-confined Pd clusters formed that can be re-dispersed upon oxidation
- Increasing the weight percentage of isolated Pd increases the amount of weakly and strongly adsorbed NO
- Low T NO desorption peak seen in TPD experiments is attributed to Pd²⁺ (NNN) sites; high T NO desorption peak seen in TPD experiments is attributed to Pd⁺H⁺ (NNN) sites
- CHA with optimized fraction of paired Al sites prepared for future work – catalyst regeneration studies will be a particular focus

Technical Back-Up Slides

In-situ Pd L₃ XANES and DRUV-Vis: Dry NO Adsorption and Desorption on Pd-CHA

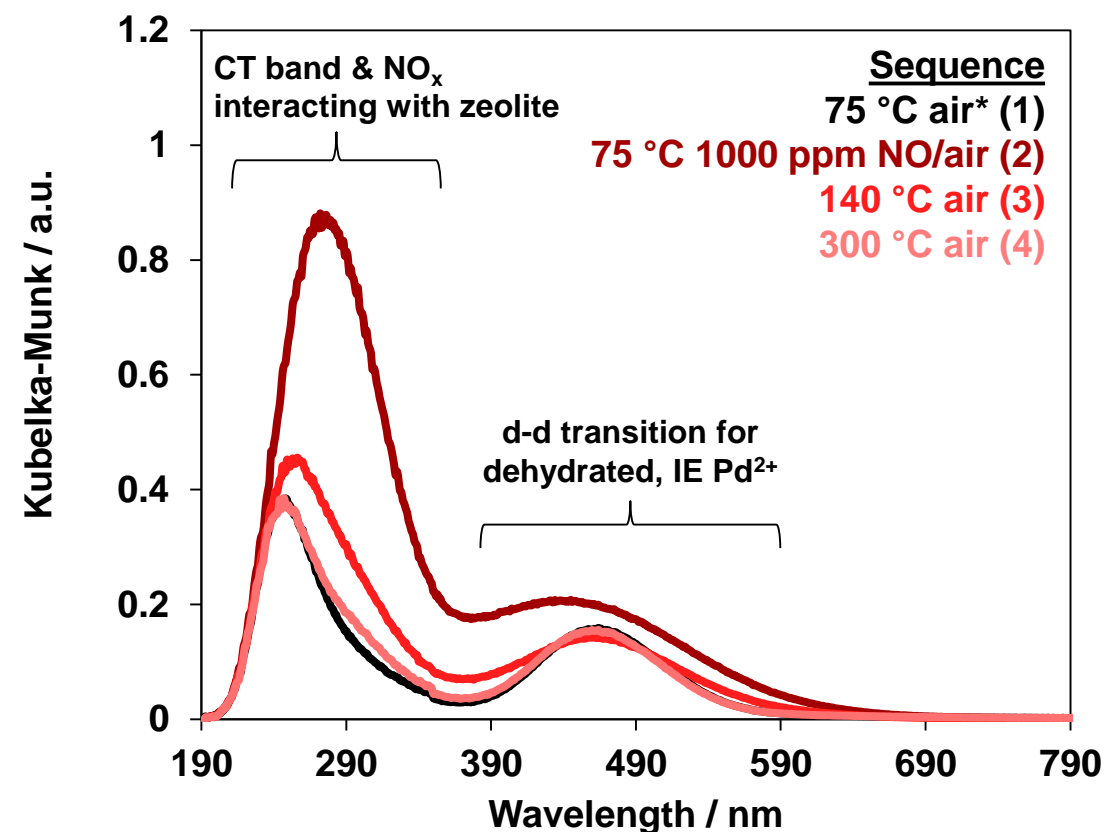
Sample composition: Si/Al = 5, Pd wt% = 1.2, Pd/Al = 0.04, IE Pd²⁺ / Pd_{tot} = 1.00 (measured with H₂ TPR)

Pd L₃ XANES



- The edge energies of all Pd L₃-edge spectra were 3174 eV, consistent with divalent Pd
- Flowing NO decreased the whiteness intensity (3175 eV), suggesting NO has ligated to dehydrated Pd²⁺ cations
- Majority of NO desorbs from Pd by 140 °C in dry air

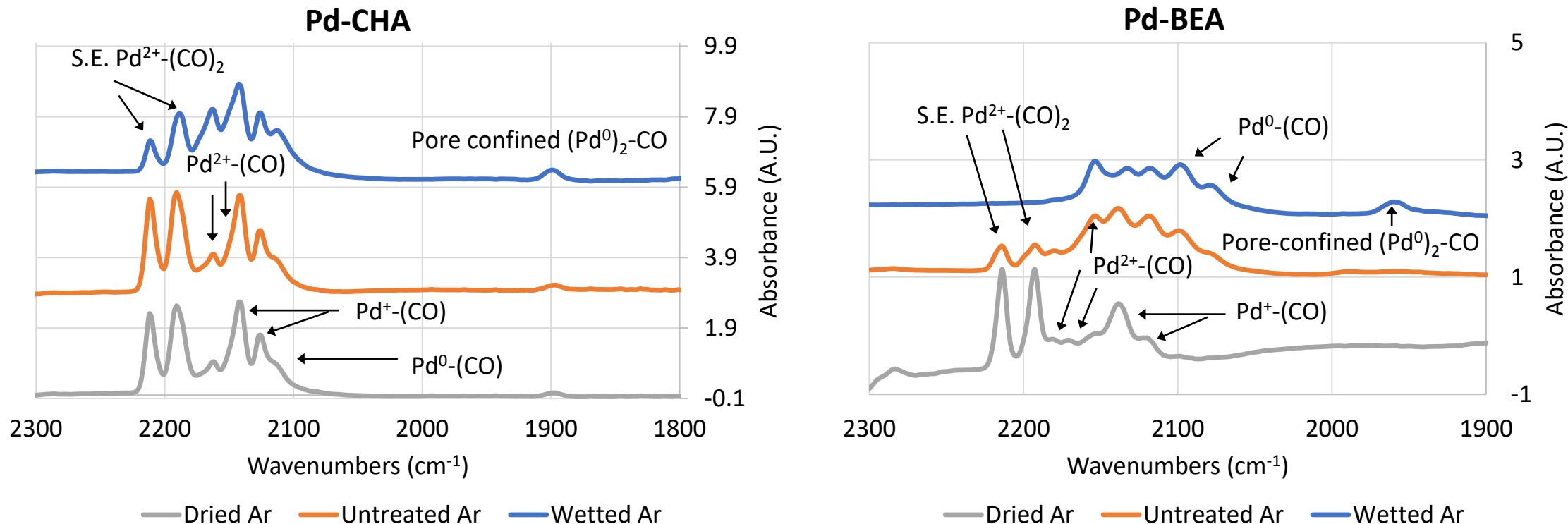
DRUV-Vis



- Flowing NO over dehydrated Pd-CHA resulted in UV-Vis absorption increases at 290 nm and 450 nm
- The absorption at 290 nm is from NO interacting with zeolite and 450 nm is from NO interacting with Pd
- Majority of NO has desorbed from Pd by 140 °C in dry air

*Sample was dehydrated in flowing air at 450 °C (10 °C min⁻¹) for 30 minutes, then cooled to 75 °C before the spectra was taken

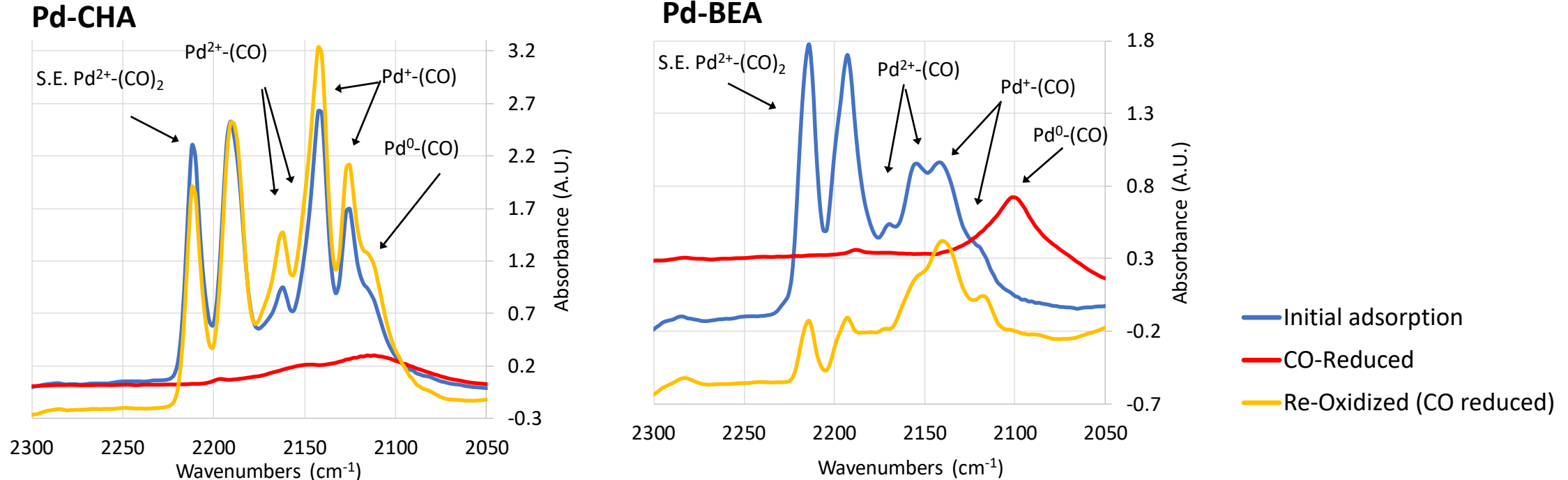
DRIFTS: Water Affects Pd-Speciation in 1% Pd-CHA and 1% Pd-BEA



Sample pretreated in dry Ar, untreated Ar, or wetted Ar at 500 °C, CO/Ar adsorbed at 25 °C for 10 min

- Water has reducing effect on both catalysts: increase in metallic Pd, decrease in ionic Pd
- Super-electrophilic Pd^{2+} eliminated by water on Pd-BEA
- $(\text{Pd}^0)_2-\text{CO}$ bands suggest pore confined Pd at 1950 cm^{-1} (Pd-BEA) and 1890 cm^{-1} (Pd-CHA)
- Pd-CHA more resilient to water exposure

Effect of Hydrogen Reduction on Pd-CHA and Pd-BEA

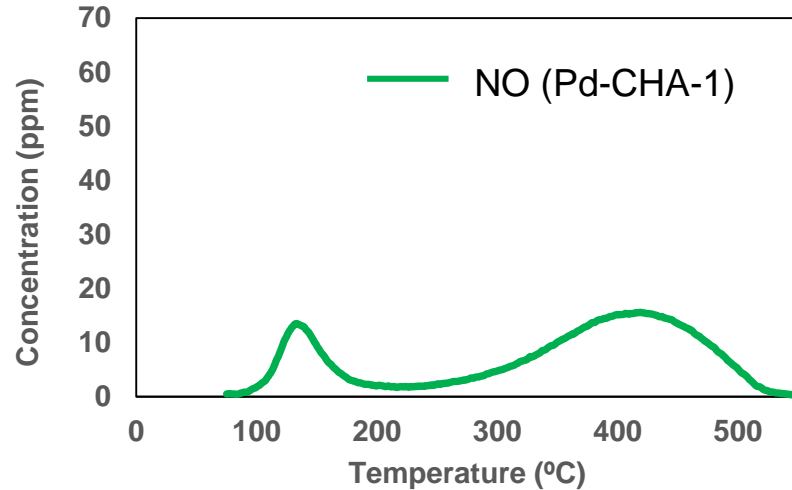


Samples treated in (i) dry Ar; (ii) 10% H_2 in Ar; (iii) dry air at 500 °C. CO adsorbed at 25 °C for 10 min

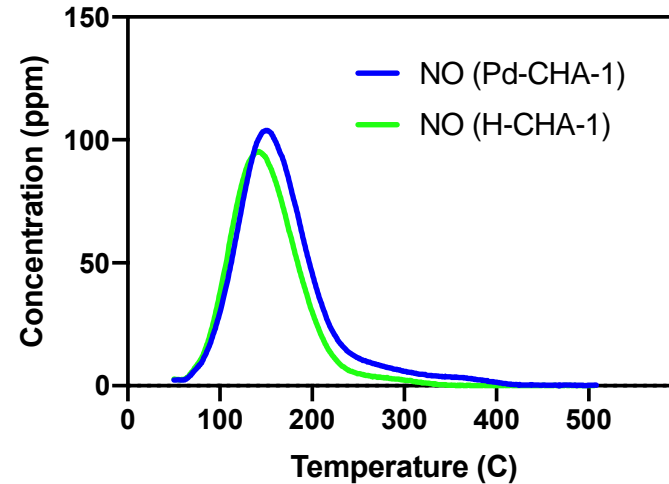
- Pd-CHA-1: increased intensity of ionic Pd after re-oxidation of H_2 -reduced sample implies reduction/redispersion of PdO initially present
- Pd-BEA: decreased intensity of ionic Pd after re-oxidation of H_2 -reduced sample implies Pd sintering
- Overall, Pd-BEA is indicated to be more sensitive to Pd sintering upon reduction than Pd-CHA

Effects of O₂ on NO Adsorption and TPD on H-CHA and Pd-CHA

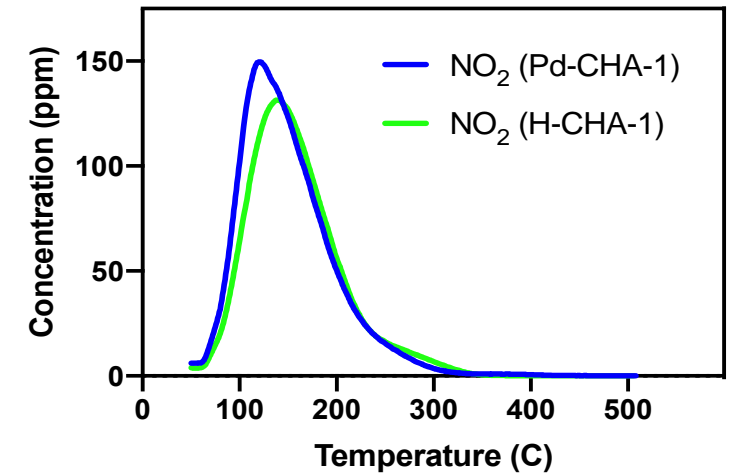
Adsorption and TPD in He



TPD - Desorption in O₂



TPD - Desorption in O₂



- NO adsorption and TPD in He results in desorption peaks at 150°C and 425°C
 - NO adsorption and desorption in O₂(5%)/He results in a single desorption peak at 150°C for H-CHA-1 and Pd-CHA-1
 - During TPD, both NO and NO₂ desorb, suggesting that in the presence of O₂, NO may adsorb as NO₂ or N₂O₄ in CHA-1
- NO can adsorb in both H-CHA and Pd-CHA
 - In H-CHA, NO adsorbs weakly and desorbs at NO at 150°C
 - In Pd-CHA, NO adsorbs weakly and strongly and desorbs at 150°C and 425°C
 - Weakly adsorbed NO in both H-CHA and Pd-CHA is displaced by water vapor
 - NO adsorption and desorption in the presence of O₂ increases the uptake of NO significantly and upon TPD desorbs as both NO and NO₂

Synthesis of CHA with Different Al Distributions

	Si (wt%)	Al (wt%)	Si/Al ₂ (molar)	Co (wt%)	Co/Al (molar)	Al at Paired Sites (wt%)	Al at Isolated Sites (wt%)	Theoret. Max. Pd (wt%)	Notes
CHA #7	42.68	4.31	19.0	0.308	0.033	0.28	4.03	0.56	6.5 wt% of Al paired
CHA #8	42.10	3.89	20.8	2.25	0.265	2.06	1.83	4.06	53.0 wt% of Al paired
CHA #9	42.87	4.02	20.5	0.475	0.054	0.43	3.59	0.86	10.8 wt% of Al paired

Samples prepared by BASF according to recipes from Purdue were exchanged with Co²⁺ at Ford (1 M cobalt acetate, 60°C for 24 h), calcined 4 h 600°C, then analyzed by XRF to obtain elemental abundance.

- XRF confirms that CHA-7, CHA-8, and CHA-9 have similar Si/Al ratios but different Co uptake, suggesting different aluminum distribution
- Washcoated monolith samples prepared for evaluation in engine exhaust